

19 Chemical thermodynamics

The gas constant, R , has the value $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$; 1 bar is 10^5 N m^{-2} ; 1 atmosphere is $1.01325 \times 10^5 \text{ N m}^{-2}$; 1 Torr is 133.3 N m^{-2} .

- 19.1 4×10^{-3} moles of an ideal gas are held inside a cylinder by a piston such that the volume of the gas is 10 cm^3 ; the whole assembly is held in a thermostat at 298 K . Calculate the pressure of the gas in N m^{-2} . [Note that the SI unit of volume is m^3 .]
- (a) Assume that the external pressure is fixed at 1 bar. Explain why the piston moves out when it is released, and why it eventually comes to a stop. What will the pressure of the gas inside the cylinder be when the piston finally stops?
 - (b) Calculate the volume of the gas inside the cylinder when the piston has come to rest, and hence the work for this irreversible expansion.
 - (c) State the change in the internal energy, ΔU , of the gas when it undergoes this isothermal expansion. Hence, using the First Law, calculate the heat associated with the expansion, explaining its sign.
 - (d) Calculate the work associated with reversible isothermal expansion between the same initial and final states as the irreversible expansion described above; hence find the heat. Comment on these values in relation to those for the irreversible expansion.
 - (e) Determine the enthalpy change of the gas in (i) the reversible and (ii) the irreversible expansion.

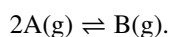
- 19.2 A sample of methane gas of mass 4.50 g has volume 12.7 dm^3 at 310 K . It expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm^3 . Assuming methane to be a perfect gas, calculate the work and heat associated with the process, along with the change in the internal energy and enthalpy of the gas. [1 Torr = 133.3 N m^{-2} .]

Calculate these same quantities if the expansion is carried out reversibly.

- 19.3 For the $A \rightleftharpoons B$ equilibrium, sketch a graph showing how the molar Gibbs energy of a mixture of A and B varies as the composition varies from pure reactant A to pure product B for the following cases: (a) $G_{\text{m,A}}^\circ = G_{\text{m,B}}^\circ$, (b) $G_{\text{m,A}}^\circ < G_{\text{m,B}}^\circ$. On your graph indicate the equilibrium composition.

Explain why it is that if the proportions of A and B are not at their equilibrium values, there is always a spontaneous process which will result in the composition moving to its equilibrium value, but that once this point is reached, no further change is possible.

- 19.4 Consider the equilibrium



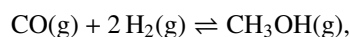
Using the approach illustrated in section 19.6.3 on page 748, show that for this reaction at equilibrium we have

$$\Delta_r G^\circ = -RT \ln K \quad \text{where} \quad K = \frac{p_{\text{B,eq}}/p^\circ}{(p_{\text{A,eq}}/p^\circ)^2},$$

and

$$\Delta_r G^\circ = G_{\text{m,B}}^\circ - 2G_{\text{m,A}}^\circ.$$

- 19.5 This question and the two which follow concern the equilibrium

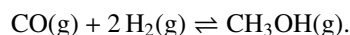


which we are going to investigate as a viable commercial method for the production of methanol. The following data are provided (all at 298 K)

	CO(g)	H ₂ (g)	CH ₃ OH(g)
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-110.53		-200.66
$S_m^\circ / \text{J K}^{-1} \text{mol}^{-1}$	197.67	130.68	239.81
$C_{p,m}^\circ / \text{J K}^{-1} \text{mol}^{-1}$	29.14	28.82	43.89

Using these data, determine $\Delta_r H^\circ$, $\Delta_r S^\circ$, $\Delta_r G^\circ$ and hence K , all at 298 K. On the basis of your answer, comment on the viability of the reaction as a method for the production of methanol.

- 19.6 In practice, it is found that the reaction in the previous question only proceeds at a viable rate at 600 K. Assuming that the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are the same at 600 K as they are at 298 K, find the value of the equilibrium constant at 600 K. Qualitatively, is your answer in accord with Le Chatelier's principle?
- 19.7 Using the approach described in section 19.8.1 on page 752 and section 19.8.2 on page 753, together with the data given in question 19.5, find the value of $\Delta_r C_p^\circ$ and hence the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ at 600 K for the equilibrium



Hence compute $\Delta_r G^\circ$ and K at 600 K. How do your values compare with those found in exercise 17.5?

- 19.8 Consider the equilibrium in which solid calcium carbonate decomposes to the oxide plus carbon dioxide



Using the approach illustrated in section 19.7.1 on page 750, show that

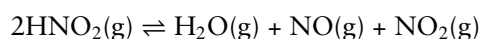
$$\Delta_r G^\circ = -RT \ln K$$

where p_{CO_2} is the equilibrium pressure of CO_2 and

$$\Delta_r G^\circ = G_m^\circ(\text{CaO}) + G_m^\circ(\text{CO}_2) - G_m^\circ(\text{CaCO}_3) \quad \text{and} \quad K = \frac{p_{\text{CO}_2}}{p^\circ}.$$

The standard enthalpies of formation of $\text{CaCO}_3\text{(s)}$, $\text{CO}_2\text{(g)}$ and CaO(s) are $-1207.6 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-634.9 \text{ kJ mol}^{-1}$ respectively, and the standard entropies are $91.7 \text{ J K}^{-1} \text{mol}^{-1}$, $213.8 \text{ J K}^{-1} \text{mol}^{-1}$ and $38.1 \text{ J K}^{-1} \text{mol}^{-1}$ (all at 298 K). Assuming that these values are independent of temperature, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 800 K; hence find the equilibrium pressure of carbon dioxide at this temperature.

19.9 Thermodynamic data, at 298 K, for the reagents and products of the gas phase reaction



are given below.

	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S_m^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$C_{p,m}^\circ / \text{J K}^{-1} \text{mol}^{-1}$
$\text{HNO}_2(\text{g})$	-79.5	254.0	45.6
$\text{H}_2\text{O}(\text{g})$	-241.8	188.7	33.6
$\text{NO}(\text{g})$	90.2	210.7	29.8
$\text{NO}_2(\text{g})$	33.2	240.0	37.2

Calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 298 K. Assuming that the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ at 548 K are the same as those at 298 K, calculate $\Delta_r G^\circ$ at 548 K.

Calculate $\Delta_r C_p^\circ$ and, using this value, compute $\Delta_r H^\circ$, $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at 548 K. Compare the two values of $\Delta_r G^\circ$ you have obtained, and comment on what is the major source of the temperature variation of $\Delta_r G^\circ$ for this reaction. Calculate K for the reaction at 298 K and at 548 K.

19.10 The standard molar entropy of N_2 gas at 298 K is $191.6 \text{ J K}^{-1} \text{mol}^{-1}$, and its standard molar constant pressure heat capacity, $C_{p,m}^\circ$, at the same temperature is $29.70 \text{ J K}^{-1} \text{mol}^{-1}$.

- Using Eq. 19.46 on page 754, find the standard molar entropy of N_2 at 398 K.
- A better approximation than assuming that $C_{p,m}^\circ$ is constant is to use a parametrized form which includes a temperature dependence. For example

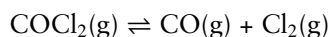
$$C_{p,m}^\circ(T) = A + BT.$$

Using this expression for $C_{p,m}^\circ$, show that integrating Eq. 19.45 on page 754 between T_1 and T_2 gives the following

$$S_m^\circ(T_2) = S_m^\circ(T_1) + A \ln\left(\frac{T_2}{T_1}\right) + B[T_2 - T_1]$$

- For N_2 $A = 28.58 \text{ J K}^{-1} \text{mol}^{-1}$ and $B = 3.77 \times 10^{-3} \text{ J K}^{-2} \text{mol}^{-1}$. Using these values in the expression above, calculate the entropy at 398 K. Comment on the difference between your answer and that obtained in (a).

19.11 The equilibrium constant, K , for the reaction



has been measured at a series of temperatures around 700 K as follows

T / K	635.7	670.4	686.0	722.2	760.2
K	0.01950	0.04414	0.07575	0.1971	0.5183

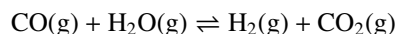
By plotting a graph of $\ln K$ against $1/T$, obtain a value for $\Delta_r H^\circ$ for the above reaction; explain any approximations you have to make. Use your graph to find a value of $\Delta_r G^\circ$ at 700 K, and hence find a value for $\Delta_r S^\circ$ at the same temperature.

- 19.12 Using the approach illustrated in section 19.9 on page 755 show that the equilibrium constants at T_1 and T_2 are related according to

$$\ln(K(T_2)) - \ln(K(T_1)) = -\frac{\Delta_r H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right].$$

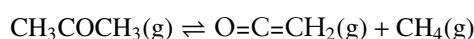
What assumptions are made in deriving this equation?

For the reaction



K is 1.038×10^5 at 298 K and 1.094×10^4 at 350 K. Use the expression above to calculate a value for $\Delta_r H^\circ$. Determine $\Delta_r G^\circ$ at 298 K, and use this value to find $\Delta_r S^\circ$ at this temperature.

- 19.13 Ketene $\text{O}=\text{C}=\text{CH}_2$ is a reactive gas which can be prepared by the thermal decomposition of propanone (acetone) vapour



Using the approach described in section 7.15 on page 250, complete the following table:

line	propanone	\rightleftharpoons	ketene	CH_4
1	n_0		0	0
2	$n_0(1 - \alpha)$			
3				

Line 1 gives the initial amount in moles, line 2 gives the amounts in moles at equilibrium, and line 3 gives the mole fractions; α is the fraction of propanone which has decomposed.

Show that the equilibrium constant can be written

$$K = \frac{\alpha^2}{(1 - \alpha)(1 + \alpha)} \frac{p_{\text{eq}}}{p^\circ},$$

where p_{eq} is the pressure of the equilibrium mixture. Using this expression, find the value of K which corresponds to 90% decomposition of propanone at a total pressure of 1.2 bar.

At 298 K, $\Delta_r G^\circ$ for this reaction is 42 kJ mol^{-1} , and $\Delta_r H^\circ$ is 81 kJ mol^{-1} . Find the value of the equilibrium constant at 298 K and then, using the relationship below, find the temperature at which there is 90% decomposition of propanone at a total pressure of 1.2 bar.

$$\ln(K(T_2)) - \ln(K(T_1)) = -\frac{\Delta_r H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$